8
Carbon

8.1 Introduction

One thing is absolutely certain — it is quite impossible to do justice to the chemistry of carbon in a single chapter; or, indeed, a single book. The areas of chemistry traditionally thought of as organic chemistry will largely be omitted except where they illuminate the general chemistry of the element. The field of organometallic chemistry is discussed in Section 19.7: this has been one of the most rapidly developing areas of the subject during the past 40 y and has led to major advances in our understanding of the structure, bonding and reactivity of molecular compounds. In fact, the unifying concepts emerging from organometallic chemistry emphasize the dangers of erecting too rigid a barrier between various branches of the subject, and nowhere is the boundary between inorganic and organic chemistry more arbitrary and less helpful than here. The present chapter gives a general account of the chemistry of carbon and its compounds; a more detailed discussion of specific organometallic systems will be found under the individual elements. Discussion of Group trends and the comparative chemistry of the Group 14 elements C, Si, Ge, Sn and Pb is deferred until Chapter 10.

Carbon was known as a substance in prehistory (charcoal, soot) though its recognition as an element came much later, being the culmination of several experiments in the eighteenth century.[1] Diamond and graphite were known to be different forms of the element by the close of the eighteenth century, and the relationship between carbon, carbonates, carbon dioxide, photosynthesis in plants, and respiration in animals was also clearly delineated by this time (see Panel). The great upsurge in synthetic organic chemistry began in the 1830s and various structural theories developed following the introduction of the concept of valency in the 1850s. Outstanding achievements in this area were F. A. Kekulé's use of structural formulae for organic compounds and his concept of the benzene ring, L. Pasteur's work on optical activity and the concept of tetrahedral carbon (J. H. van't Hoff).[†]

---

[1] M. E. WEEKS, *Discovery of the Elements*, Chaps. 1 and 2, pp. 58–89. J. Chem. Educ. Publ., 1956.

[†] J. A. Le Bel, whose name is often also associated with this concept, did indeed independently suggest a 3-dimensional model for the 4-coordinate C atom, but vigorously opposed the tetrahedral stereochemistry of van't Hoff for many years and favoured an alternative square pyramidal arrangement of the bonds.

Early History of Carbon and Carbon Dioxide

	Carbon known as a substance in prehistory (charcoal, soot) but not recognized as an element until the second half of the eighteenth century.
BC	"Indian inks" made from soot used in the oldest Egyptian hieroglyphs on papyrus.
AD 1273	Ordinance prohibiting use of coal in London as prejudicial to health — the earliest known attempt to reduce smoke pollution in Britain.
~1564	Lead pencils first manufactured commercially during Queen Elizabeth's reign, using Cumberland graphite.
1752/4	CO_2 ("fixed air"), prepared by Joseph Black (aged 24–26), was the first gas other than air to be characterized: (i) chalk when heated lost weight and evolved CO_2 (genesis of quantitative gravimetric analysis), and (ii) action of acids on carbonates liberates CO_2.
1757	J. Black showed that CO_2 was produced by fermentation of vegetables, by burning charcoal and by animals (humans) when breathing; turns lime water turbid.
1771	J. Priestley established that green plants use CO_2 and "purify air" when growing. He later showed that the "purification" was due to the new gas oxygen (1774).
1779	Elements of photosynthesis elucidated by J. Ingenhousz: green plants in daylight use CO_2 and evolve oxygen; in the dark they liberate CO_2.
1789	The word "carbon" (Fr. *carbone*) coined by A. L. Lavoisier from the Latin *carbo*, charcoal. The name "graphite" was proposed by A. G. Werner and D. L. G. Harsten in the same year: Greek γραφίεν (*graphein*), to write. The name "diamond" is probably a blend of Greek δίαφανής (*diaphanes*), transparent, and αδαμας (*adamas*), indomitable or invincible, in reference to its extreme hardness.
1796	Diamond shown to be a form of carbon by S. Tennant who burned it and weighed the CO_2 produced; graphite had earlier been shown to be carbon by C. W. Scheele (1779); carbon recognized as essential for converting iron to steel (R.-A.-F de Réaumur and others in the late eighteenth century).
1805	Humphry Davy showed carbon particles are the source of luminosity in flames (lamp black).

The first metal carbonyl compounds $Ni(CO)_4$ and $Fe(CO)_5$ were prepared and characterized by L. Mond and his group in 1889–91 and this work has burgeoned into the huge field of metal carbonyl cluster compounds which is still producing results of fundamental importance. Even more extensive is the field of organometallic chemistry which developed rapidly after the seminal papers on the "sandwich" structure of ferrocene (E. O. Fischer and W. Pfab, 1952; G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, 1952) and the "π bonding" of ethylene complexes (M. J. S. Dewar 1951, J. Chatt, and L. A. Duncanson, 1953). The constricting influence of classical covalent-bond theory was finally overcome when it was realized that carbon in many of its compounds can be 5-coordinate (Al_2Me_6, p. 258), 6-coordinate ($C_2B_{10}H_{12}$, p. 185) or even 7-coordinate (Li_4Me_4, p. 104). A compound featuring an 8-coordinate carbon atom is shown on p. 1142. In parallel with these developments in synthetic chemistry and bonding theory have been technical and instrumental advances of great significance; foremost amongst these have

been the development of ^{14}C radioactive dating techniques (W. F. Libby, 1949), the commercial availability of ^{13}C nmr instruments in the early 1970s, and the industrial production of artificial diamonds (General Electric Company, 1955). These and other notable dates in carbon chemistry are summarized in the Panel on p. 270.

The most exciting recent development in the chemistry of carbon has been the intriguing discovery of a whole new range of soluble molecular forms of elemental carbon, the fullerenes, of which C_{60} and C_{70} are the most prominent members. This was recognized by the 1996 Nobel Prize for Chemistry and has stimulated an enormous amount of research which is discussed in Section 8.2.4 (p. 279).

8.2 Carbon

8.2.1 Terrestrial abundance and distribution

Carbon occurs both as the free element (graphite, diamond) and in combined form (mainly as the

Some Notable Dates in Carbon Chemistry

1807	J. J. Berzelius classified compounds as "organic" or "inorganic" according to their origin in living matter or inanimate material.
1825–7	W. C. Zeise prepared $K[Pt(C_2H_4)Cl_3]$ and related compounds; though of unknown structure at the time they later proved to be the first organometallic compounds.
1828	The vitalist theory of Berzelius challenged by F. Wöhler (aged 28) who synthesized urea, $(NH_2)_2CO$, from $NH_4(OCN)$.
1830+	Rise of synthetic organic chemistry.
1848	L. Pasteur (aged 26) began work on optically active sodium ammonium tartrate.
1849	First metal alkyls, e.g. $ZnEt_2$, made by E. Frankland (aged 24); he also first propounded the theory of valency (1852).
1858	F. A. Kekulé's structural formulae for organic compounds; ring structure of benzene 1865.
1874	Tetrahedral, 4-coordinate carbon proposed by J. H. van't Hoff (aged 22) see also footnote to p. 268.
1890	First paper on metal carbonyls $[Ni(CO)_4]$ by L. Mond, C. Langer and F. Quincke.
1891	Carborundum, SiC, made by E. G. Acheson.
1900	First paper by V. Grignard (aged 29) on RMgX syntheses. Nobel Prize 1912.
1924	Solid CO_2 introduced commercially as a refrigerant.
1926	C_8K prepared — the first alkali metal-graphite intercalation compound.
1929	Isotopes of C (^{12}C and ^{13}C) discovered by A. S. King and R. T. Birge in the band spectrum of C_2, CO and CN (previously undetected by mass spectrometry).
1932	First metal halide-graphite intercalation compound made with $FeCl_3$.
1936	Radiocarbon $^{14}_6C^*$ established as the product of an (n,p) reaction on $^{14}_7N$ by W. E. Burcham and M. Goldhaber.
1940	Chemically significant amounts of ^{14}C synthesized by S. Ruben and M. D. Kamen.
1947–9	Concept and feasibility of ^{14}C dating established by W. F. Libby (awarded Nobel Prize in 1960).
1952	Structure of ferrocene elucidated; organometallic chemistry burgeons: Nobel Prize awarded jointly to E. O. Fischer and G. Wilkinson 1973.
1953	First authentic production of artificial diamonds by ASEA, Sweden; commercial production achieved by General Electric (USA) in 1955.
1955	Stereoregular polymerization of ethene and propene by catalysts developed by K. Ziegler and by G. Natta (shared Nobel Prize 1963).
1956	Cyclobutadiene–transition metal complexes predicted by H. C. Longuet-Higgins and L. E. Orgel 3 y before they were first synthesized.
1960	π-allylic metal complexes first recognized.
1961	$^{12}C = 12$ internationally adopted as the unified atomic weight standard by both chemists and physicists.
1964	6-coordinate carbon established in various carboranes by W. N. Lipscomb and others. (Nobel Prize 1976 for structure and bonding of boranes).
1965	Mass spectrometric observation of CH_5^+ by F. H. Field and M. S. B. Munson, and subsequent extensive study of hypercoordinate C compounds by G. A. Olah *et al.*
1966	CS_2 complexes such as $[Pt(CS_2)(PPh_3)_2]$ first prepared in G. Wilkinson's laboratory.
1971	^{13}C fourier-transform nmr commercially available following first observation of ^{13}C nmr signal by P. C. Lauterbur and by C. H. Holm in 1957.
1976	8-coordinate carbon established in $[Co_8C(CO)_{18}]^{2-}$ by V. G. Albano, P. Chini *et al.* (Cubic coordination of C in the antifluorite structure of Be_2C known since 1948.)
1985	Discovery of C_{60} and C_{70} molecules (fullerenes) by H. Kroto, R. E. Smalley and their colleagues.
1989	Large-scale synthesis of C_{60} and C_{70} by D. Huffmann and W. Krätschmer.
1994	Nobel Prize to G. A. Olah for contributions to carbocation chemistry.
1996	Nobel Prize to R. Curl, H. Kroto and R. E. Smalley for discovery of the fullerenes.

carbonates of Ca, Mg and other electropositive elements). It also occurs as CO_2 a minor but crucially important constituent of the atmosphere. Estimates of the overall abundance of carbon in crustal rocks vary considerably, but a value of 180 ppm can be taken as typical; this places the element seventeenth in order of abundance after Ba, Sr and S but before Zr, V, Cl and Cr.
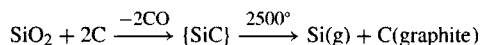
Graphite is widely distributed throughout the world though much of it is of little economic importance. Large crystals or "flake" occur in metamorphosed sedimentary silicate rocks such as quartz, mica schists and gneisses; crystal size varies from <1 mm up to about 6 mm (average ~4 mm) and the deposits form lenses up to 30 m thick stretching several

Production and Uses of Graphite[2]

There is a world shortage of natural graphite which is particularly marked in North America and Europe. As a result, prices have risen steeply; they vary widely in the range $500–1500 per tonne (1989) depending on crystalline quality; "amorphous" graphite is $220–440 per tonne. The annual world production of 649 ktonnes was distributed as follows in 1988: China 200 kt, South Korea 108, the former Soviet Union 84, India 52, Mexico 42, Brazil 32, North Korea 25, Czechoslovakia 25, Others 81 kt.

The USA used 37 ktonnes of natural graphite in 1989, nearly all imported; in addition, over 300 ktonnes of graphite was manufactured. Natural graphite is used in refractories (27%), lubricants (17%), foundries (14%), brake linings (12%), pencils (5.3%), crucibles, retorts, stoppers, sleeves and nozzles (4.0%) etc.

Artificial graphite was first manufactured on a large scale by A. G. Acheson in 1896. In this process coke is heated with silica at ~2500°C for 25–35 h:

$$SiO_2 + 2C \xrightarrow{\ -2CO\ } \{SiC\} \xrightarrow{\ 2500°\ } Si(g) + C(graphite)$$

In the USA artificial graphite is now made on a scale exceeding 300 kilotonnes pa (1989), and is used mainly for electrodes, crucibles and vessels, and various unmachined shapes; specialist uses include motor brushes and contacts and refractories of various sorts.

Carbon (graphite) fibres are also being manufactured on an increasing scale: The global market (1990) is of the order of 6 million kg per annum and prices range from $20–2000/kg depending on specifications (diameter, strength, stiffness, etc.). The two main production methods are the oxidative thermolysis of polyacrilonitrile fibres at 200–300°C under tension or the thermolysis of pitch at 370° followed by die-extrusion and stretching to give filaments which are then heated progressively in dry air to 2500°. Ultra-high-purity graphite is made on a substantial scale for use as a neutron moderator in nuclear reactors. Carbon whiskers grown from highly purified graphite are finding increasing use in high-strength composites; the whiskers are manufactured by striking a carbon arc at 3600°C under 90 atm Ar — the maximum length is ~50 mm and the average diameter 5 μm.

kilometres across country. Average carbon content is 25% but can rise as high as 60% (Malagasy). Beneficiation is by flotation followed by treatment with HF and HCl, and then by heating to 1500°C *in vacuo*. Microcrystalline graphite (sometimes referred to as "amorphous") occurs in carbon-rich metamorphosed sediments and some deposits in Mexico contain up to 95% C. World production has remained fairly constant for the past few years and was 649 ktonnes in 1988 (see Panel above).

Diamonds are found in ancient volcanic pipes embedded in a relatively soft, dark coloured basic rock called "blue ground" or "kimberlite", from the South African town of Kimberley where such pipes were first discovered in 1870. Diamonds are also found in alluvial gravels and marine terraces to which they have been transported over geological ages by the weathering and erosion of pipes. The original mode of formation of the diamond crystals is still a subject of active investigation. The diamond content of a typical kimberlite pipe is extremely low, of the order of 1 part in 15 million, and the mineral must be isolated mechanically by crushing, sluicing and passing the material over greased belts to which the diamonds stick. This, in part, accounts for the very high price of gem-quality diamonds which is about 1 million times the price of flake graphite. The pattern of world production has changed dramatically over the past few decades as indicated in the Panel on p. 272.

Three other forms of carbon are manufactured on a vast scale and used extensively in industry: coke, carbon black, and activated carbon. The production and uses of these impure forms of carbon are briefly discussed in the Panel on p. 274.

In addition to its natural occurrence as the free element, carbon is widely distributed in the

[2] *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th edn., Interscience, New York, 1992, Vol. 4: Carbon and artificial graphite, pp. 949–1015; Activated carbon, pp. 1015–37; Carbon black, pp. 1037–74; Diamond, natural and synthetic, pp. 1074–96; Natural graphite, pp. 1097–117; Carbon and graphite fibres, vol 5, pp. 1–19 (1993). See also H. O. PIERSON, *Handbook of Carbon, Graphite, Diamond and Fullerenes: Properties, Processing and Applications*, Noyes Publications, Park Ridge, N.J., 1993, 399 pp.

Production and Uses of Diamond[2, 2a]

Gemstone diamonds have been greatly prized in eastern countries for over 2000 y though their introduction and recognition in Europe is more recent. The only sources were from India and Borneo until they were also found in Brazil in 1729. In South Africa diamonds were discovered in alluvial deposits in 1867 and the first kimberlite pipe was identified in 1870 with dramatic consequences. Many other finds of economic importance were made in Africa during the first half of this century: most notably in Tanzania where large-scale production began in 1940 following the discovery of the enormous Williamson pipe — still the largest in the world and covering an area of $1.4\,km^2$. During the 1950s 99% of the world output of diamonds was from Africa but then the USSR began to emerge as a major producer following the discovery of alluvial diamonds in Siberia in 1948 and the first kimberlite-type pipe at Yakutia later the same year. Within a decade more than 20 pipes had been located in the great basin of the Vilyui River 4000 km east of the Urals, and Siberia was established as a major producer of both gem-quality and industrial diamonds. However, year-round production in Siberian conditions posed severe developmental problems, and production is now supplemented by newer finds in the Urals near Sverdlovsk. Impressive finds of kimberlite pipes have also been made in North-western Australia since 1978 and this area is now one of the world's largest producers of industrial diamonds.

Diamond is the hardest and least perishable of all minerals, and these qualities, coupled with its brilliant sparkle, which derives from its transparency and high refractive index, make it the most prized of gemstones. By far the largest natural diamond ever found (25 January 1905) was the Cullinan; it weighed 3106 carats (621.2 g) and measured $\sim 10 \times 6.5 \times 5\,cm^3$ (the size of a man's clenched fist). Other famous stones are in the range 100–800 carats though specimens larger than 50 carats are only rarely encountered. Most naturally occurring diamonds, however, are of industrial rather than gem-stone quality. They are used as single-point tools for engraving or cutting, and for surgical knives, bearings and wire dies, as well as for industrial abrasives for grinding and polishing. Other uses are as thermistors and radiation detectors, and as optical windows for lasers, etc.

Since the late 1950s the supply of natural diamonds has been progressively augmented by diamonds synthesized at high pressures and temperatures (p. 278) and this source now accounts for 90% of all industrial diamonds. The price for such diamond grit is relatively low, about \$5–25 per g, the higher prices being for the largest crystals (0.3–1 mm on edge). Total world production (1990) approached 100 tonnes (500 megacarats) and was worth about \$10^9. In 1985, Sumitomo Electric (Japan) began commercial production of diamond crystals of up to 2 carats (as large as 8 mm in length) and de Beer's (South Africa) have made single crystals up to 17 mm long. Such diamonds, which are pale yellow due to nitrogen inclusions, are used as heat sinks in the electronics industry because of the very high thermal conductivity of diamond. The synthetic stones are machined and laser cut to about $3 \times 3 \times 1\,mm^3$ and are commercially available for \$150 a piece. Synthetic industrial diamonds are manufactured in 16 countries, the major producers being in USA, Japan, China and Russia.
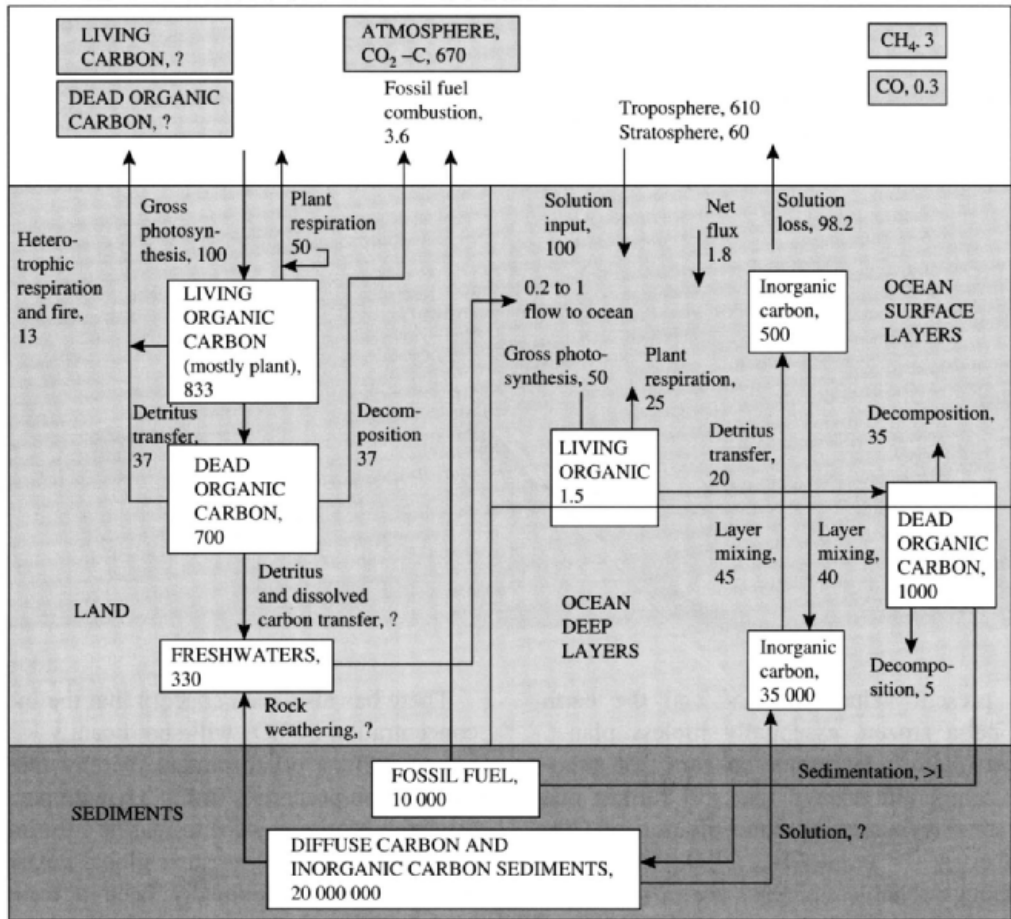
Exciting developments are also occurring in the emerging technology of large-area thin films of synthetic diamond. Such films are of interest as heat sinks for components in the electronics industry and, when bonded to inexpensive non-diamond surfaces, can also provide the unexcelled hardness, wear resistance and chemical inertness of diamond at lower cost than that of the bulk element. The films are made by low pressure (50 mbar) chemical vapour deposition of metastable diamond at 1000°C, the crucial feature of the method being the simultaneous presence of a plasma of atomic H to prevent the concurrent deposition of graphite from the decomposing organic vapours (see p. 278).

---

form of coal and petroleum, and as carbonates of the more electropositive[†] elements (e.g. Group 1, p. 88, Group 2, pp. 109, 122). The great bulk of carbon is immobilized in the form of coal, limestone, chalk, dolomite and other deposits, but there is also a dynamic equilibrium as a result of the numerous natural processes which constitute the so-called carbon cycle. The various

reservoirs of carbon and the flow between them are illustrated in Fig. 8.1 from which it is clear that there are two distinct cycles — one on land and one in the sea, dynamically inter-connected by the atmosphere. CO_2 in the atmosphere ($\sim 6.7 \times 10^{11}$ tonnes) accounts for only 0.003% of carbon in the earth's crust ($\sim 2 \times 10^{16}$ tonnes). It is in rapid circulation with the biosphere being removed by plant photosynthesis and added to by plant and animal respiration, and the decomposition of dead organic matter; it is also produced by the activities of man, notably the combustion of fossil fuels for energy and the calcination of limestone for cement. These last

---

[2a] R. M. HAZEN, *The New Alchemists: Breaking Through the Barriers of High Pressure*, Times Books, New York, 1994, 286 pp. P. W. MAY, *Endeavour* **19**, 101–6 (1995).

[†] Note that the *weight* of diamonds is usually quoted in carats (1 carat = 0.200 g); this unit is quite different from the carat used to describe the *quality* of gold (p. 1176).

Figure 8.1   Diagrammatic model of the global carbon cycle. Questions marks indicate that no estimates are available. Figures are in units of 10^9 tonnes of contained carbon but estimates from various sources sometimes differ by factors of 3 or more. The diagram is based on one by B. Bolin[3] modified to include more recent data.[4]

two activities have increased dramatically in recent years and give some cause for concern. Interchange on a similar scale occurs between the atmosphere and ocean waters, and the total residence time of CO_2 in the atmosphere is $\sim$10–15 y (as measured by ^{14}C experiments).

An increase in the concentration of atmospheric CO_2 has been thought by some to expose the planet to the dangers of a "greenhouse effect" whereby the temperature is raised due to the trapping of the earth's thermal radiation by infrared absorption in the CO_2 molecules. In fact, the greenhouse gases, especially water vapour and CO_2, play a crucial role in regulating the temperature of the earth and its atmosphere. In the absence of these gases the average surface temperature would be $-18°C$ instead

---

[3] B. BOLIN, The carbon cycle, *Scientific American*, September 1970, reprinted in *Chemistry in the Environment*, pp. 53–61, W. H. Freeman, San Francisco, 1973.

[4] *SCOPE Report 10 on Environmental Issues*, Carbon, pp. 55–8, Wiley, New York, 1977. SCOPE is the Scientific Committee on Problems of the Environment; it reports to ICSU, the International Council of Scientific Unions.

Production and Uses of Coke, Carbon Black and Activated Carbon[2]

The high-temperature carbonization of coal yields metallurgical coke, a poorly graphitized form of carbon; most of this (92%) is used in blast furnaces for steel manufacture (p. 1072). World production of coke is of the order of 400 million tonnes per annum and was dominated, as expected, by the large industrial nations. Carbon black (soot) is made by the incomplete combustion of liquid hydrocarbons or natural gas; the scale of operations is enormous, world production in 1992 being nearly 7 million tonnes. The particle size of carbon black is exceedingly small ($0.02-0.30\,\mu$m) and its principal application (90%) is in the rubber industry where it is used to strengthen and reinforce the rubber in a way that is not completely understood. For example, each car tyre uses 3 kg carbon black and each truck tyre $\sim$9 kg. Its other main uses are as a pigment in plastics (4.4%) in printing inks (3.6%) and paints (0.7%).

Activated carbons, being highly specialized products, are produced on a correspondingly smaller scale. World production capacity in 1990 being some 400 kilotonnes (USA 146, Western Europe 108, Japan 72 kt). They are distinguished by their enormous surface area which is typically in the range $300-2000\,m^2\,g^{-1}$. Activated carbon can be made either by chemical or by gas activation. In chemical activation the carbonaceous material (sawdust, peat, etc.) is mixed or impregnated with materials which oxidize and dehydrate the organic substrate when heated to 500–900°, e.g. alkali metal hydroxides, carbonates or sulfates, alkaline earth metal chlorides, carbonates or sulfates, $ZnCl_2$, H_2SO_4 or H_3PO_4. In gas activation, the carbonaceous matter is heated with air at low temperature or with steam, CO_2 or flue gas at high temperature (800–1000°).

Activated carbon is used extensively in the sugar industry as a decolorizing agent and this accounts for some 20% of the output; related applications are in the purification of chemicals and gases including air pollution (15%), and in water and waste water treatment (50%). Notable catalytic uses are the aerial oxidation in aqueous solutions of Fe^{II}, $[Fe^{II}(CN)_6]^{4-}$, $[As^{III}O_3]^{3-}$ and $[N^{III}O_2]^-$, the manufacture of $COCl_2$ from CO and Cl_2, and the production of SO_2Cl_2 from SO_2 and Cl_2. The cost of activated carbon (USA, 1990) was $0.70–5.50 per kg depending on the grade.

of the present value of $+15°$ and the earth would be a frozen, essentially lifeless planet. However, there is legitimate concern that atmospheric temperatures may rise still further due to the steadily increasing concentration of CO_2 and other gases (e.g. CH_4, N_2O, CFCs and O_3) although reliable estimates are extraordinarily difficult to obtain and depend sensitively on the computer modelling of the many interacting effects.[5] Perhaps the most reliable estimate is that there will be a temperature rise from the greenhouse effect of $1.5 \pm 1.0°C$ and a resulting average rise in sea level of 20 ± 14 cm by the year AD 2030, though even this assumes that other unrelated effects of potentially similar magnitude will not occur. The best estimates of all the various counterbalancing effects leads to the conclusion that the change in sea level will probably not exceed ± 10 cm during the next century.

There has also been concern that the increased concentration of CO_2 will significantly lower the pH of surface ocean waters thereby modifying the solution properties of $CaCO_3$ with potentially disastrous consequences to marine life. Informed opinion now discounts such global catastrophes but there has undoubtedly been a measurable perturbation of the carbon cycle in the last few decades, and the prudent course is to conserve resources, minimize wasteful practices and improve efficiency, whilst simultaneously collecting reliable data on the magnitude of the various carbon-containing reservoirs and the rates of transfer between them.[6]

8.2.2 Allotropic forms

Carbon can exist in at least 6 crystalline forms in addition to the many newly prepared fullerenes described in Section 8.2.4: α- and β-graphite, diamond, Lonsdaleite (hexagonal

[5] THE ROYAL SOCIETY (LONDON), *The Greenhouse Effect: the scientific basis for policy*, Submission to the House of Lords Select Committee, 40 pp. (1989). See also *Global Climate Change*, Information Pamphlet (12 pp.) issued by the American Chemical Society (1990); B. HILEMAN, Global Warming, *Chem. & Eng. News*, April 27, 7–19 (1992); and references cited therein.

[6] B. BOLIN, B. R. DÖÖS, J. JÄGER and R. A. WARRICK (eds.), SCOPE 29, *The Greenhouse Effect, Climatic Change and Ecosystems*, 2nd edn., 1989, 574 pp.

diamond), chaoite, and carbon(VI). Of these, α-
(or hexagonal) graphite is thermodynamically the
most stable form at normal temperatures and
pressures. The various modifications differ either
in the coordination environment of the carbon
atoms or in the sequence of stacking of layers
in the crystal. These differences have a profound
effect on both the physical and the chemical
properties of the element.

Graphite is composed of planar hexagonal nets
of carbon atoms as shown in Fig. 8.2. In normal
α- (or hexagonal) graphite the layers are arranged
in the sequence $\cdots ABAB \cdots$ with carbon
atoms in alternate layers vertically above each
other, whereas in β- (or rhombohedral) graphite
the stacking sequence is $\cdots ABCABC \cdots$. In
both forms the C–C distance within the layer
is 141.5 pm and the interlayer spacing is
much greater, 335.4 pm. The two forms are
interconvertible by grinding ($\alpha \rightarrow \beta$) or heating
above 1025°C ($\beta \rightarrow \alpha$), and partial conversion

leads to an increase in the average spacing
between layers; this reaches a maximum of
344 pm for turbostratic graphite in which the
stacking sequence of the parallel layers is
completely random. The enthalpy difference
between α- and β-graphite is only $0.59 \pm$
$0.17 \, kJ \, mol^{-1}$.

In diamond, each C atom is tetrahedrally
surrounded by 4 equidistant neighbours at
154.45 pm, and the tetrahedra are arranged to
give a cubic unit cell with a_0 356.68 pm as
in Fig. 8.3. Note that, although the diamond
structure itself is not close-packed, it is built
up of 2 interpenetrating fcc lattices which are
off-set along the body diagonal of the unit
cell by one-quarter of its length. Nearly all
naturally occurring diamonds ($\sim$98%) are of this
type but contain, in addition, a small amount
of nitrogen atoms (0.05–0.25%) in platelets of
approximate composition C_3N (type Ia) or, very
occasionally ($\sim$1%), dispersed throughout the
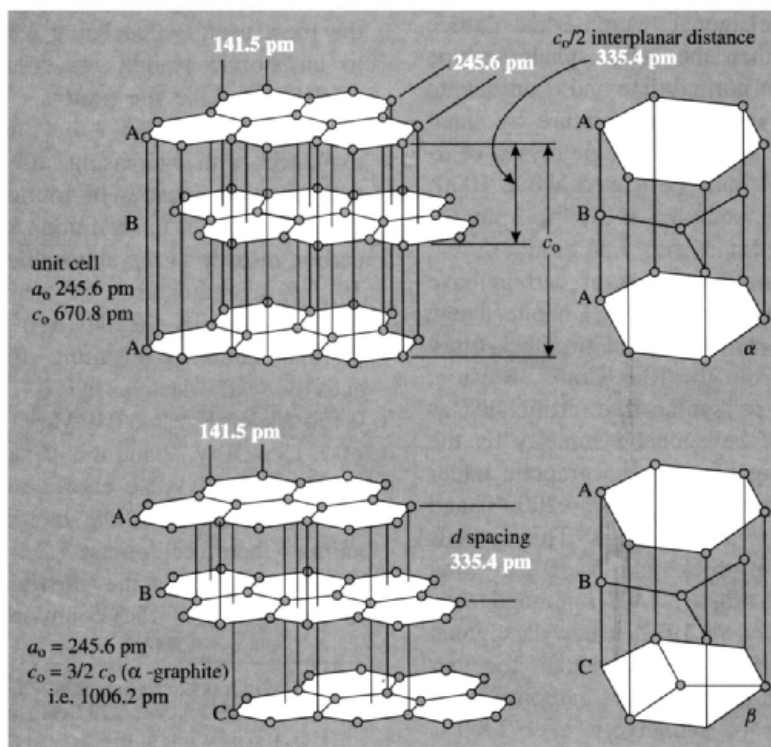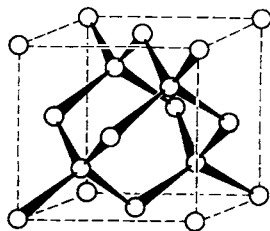

Figure 8.2   Structure of the α (hexagonal) and β (rhombohedral) forms of graphite.

Figure 8.3 Structure of diamond showing the tetrahedral coordination of C; the dashed lines indicate the cubic unit cell containing 8 C atoms.

crystal (type Ib). A small minority of natural diamonds contain no significant amount of N (type IIa) and a very small percentage of these (including the highly valued blue diamonds, type IIb), contain Al. The exceedingly rare hexagonal modification of diamond, Lonsdaleite, was first found in the Canyon Diablo Meteorite, Arizona, in 1967: each C atom is tetrahedrally coordinated but the tetrahedra are stacked so as to give a hexagonal wurtzite-like lattice (p. 1210) rather than the cubic sphalerite-type lattice (p. 1210) of normal diamond. Lonsdaleite can be prepared at room temperature by static pressure along the *c*-axis of a single crystal of α-graphite, though it must be heated above 1000° under pressure to stabilize it (a_o 252 pm, c_o 412 pm, d_{obs} 3.3 g cm^{-3}, d_{calc} 3.51 g cm^{-3}).

Two other crystalline forms of carbon have been discovered in the recent past. Chaoite, a new white allotrope, was first found in shock-fused graphitic gneiss from the Ries Crater, Bavaria, in 1968; it can be synthesized artificially as white dendrites of hexagonal symmetry by the sublimation etching of pyrolytic graphite under free vaporization conditions above ∼2000°C and at low pressure (∼10^{-4} mmHg). The crystals were only 0.5 μm thick and 5–10 μm long and had a_o 894.5 pm, c_o 1407.1 pm and d_{calc} 3.43 g cm^{-3}. Finally, in 1972, a new hexagonal allotrope, carbon(VI), was obtained together with chaoite when graphitic carbons were heated resistively or radiatively at ∼2300°C under any pressure of argon in the range 10^{-4} mmHg to 1 atm; laser heating was even

more effective (a_o 533 pm, c_o 1224 pm, $d >$ 2.9 g cm^{-3}). The detailed crystal structures of chaoite and carbon(VI) have not yet been determined but they appear to be based on a carbyne-type motif $—C{\equiv}C—C{\equiv}C;$[7] both are much more resistant to oxidation and reduction than graphite is and their properties are closer to those of diamond. Indeed, it now seems possible that there is a sequence of at least 6 stable carbyne allotropes in the region between stable graphite and the mp of carbon.

The structural differences between graphite and diamond are reflected in their differing physical and chemical properties, as outlined in the following sections.

8.2.3 Atomic and physical properties

Carbon occurs predominantly as the isotope ^{12}C but there also is a small amount of ^{13}C; the concentration of ^{13}C varies slightly from 0.99 to 1.15% depending on the source of the element, the most usual value being 1.10% which leads to an atomic weight for "normal" carbon of 12.0107(8). Like the proton, ^{13}C has a nuclear spin quantum number $I = \frac{1}{2}$, and this has been exploited with increasing effectiveness during the past two decades in fourier transform nmr spectroscopy.[8] In addition to ^{12}C and ^{13}C, carbon dioxide in the atmosphere contains 1.2×10^{-10}% of radioactive ^{14}C which is continually being formed by the $^{14}_{7}$N(n,p)$^{14}_{6}$C reaction with thermal neutrons resulting from cosmic ray activity. ^{14}C decays by β^- emission (E_{max} 0.156 MeV, E_{mean} 0.049 MeV) with a half-life of 5715 ± 30 y,[9] and this is sufficiently long to enable a steady-state equilibrium concentration to be established in the biosphere. Plants and animals therefore contain 1.2×10^{-10}% of their carbon as ^{14}C whilst they are living, and this leads to a β-activity of 15.3 counts per min per gram

[7] A. G. WHITTAKER, *Science* **200**, 763–4 (1978). See also Anon, *Chem. & Eng. News*, 29 Sept., p. 12 (1980).

[8] H.-O. KALINOWSKI, S. BERGER and S. BRAUN, *Carbon-13 NMR Spectroscopy*, Wiley, Chichester, 1988.

[9] N.E. HOLDEN, *Pure Appl. Chem.* **62**, 941–58 (1990).

of contained C. However, after death the dynamic interchange with the environment ceases and the ^{14}C concentration decreases exponentially. This is the basis of W. F. Libby's elegant radio-carbon dating technique for which he was awarded the Nobel Prize for Chemistry in 1960. It is particularly valuable for archeological dating.[10] (A modern variant is to count the number of ^{14}C atoms directly in a mass spectrometer.) The practical limit is about 50 000 y since by this time the ^{14}C activity has fallen to about 0.2% of its original valuable and becomes submerged in the background counts. ^{14}C is also extremely valuable as a radioactive tracer for mechanistic studies using labelled compounds, and many such compounds, particularly organic ones, are commercially available (p. 310).

Carbon is the sixth element in the periodic table and its ground-state electronic configuration is $[He]2s^22p^2$. The first 4 ionization energies of C are 1086.5, 2352.6, 4620.5 and 6222.7 kJ mol^{-1}, all much higher than those for the other Group 14 elements Si, Ge, Sn and Pb (p. 372). Excitation energies from the ground-state to various low-lying electron configurations of importance in valence theory are also well established:

Configuration	$2s^22p^2$	$2s^22p^2$	$2s^22p^2$
Term symbol	^3P	^1D	^1S
Energy/kJ mol^{-1}	0.000	121.5	258.2
Configuration	$2s^12p^3$	$2s^12p^3$	
Term symbol	$^5S°$	$^5S_{valence\ state}$	
Energy/kJ mol^{-1}	402.3	~632	

Of these, all are experimentally observable except the $^5S_{valence\ state}$ level which is a calculated value for a carbon atom with 4 unpaired and uncorrelated electron spins; this is a hypothetical state, not amenable to experimental observation, but is helpful in some discussions of bond energies and covalent bonding theory.

The electronegativity of C is 2.5, which is fairly close to the values for other members of the group (1.8–1.9) and for several other elements: B, As (2.0); H, P (2.1); Se (2.4); S, I (2.5); many of the second- and third-row transition metals also have electronegativities in the range 1.9–2.4.

The "single-bond covalent radius" of C can be taken as half the interatomic distance in diamond, i.e. $r(C) = 77.2$ pm. The corresponding values for "doubly-bonded" and "triply-bonded" carbon atoms are usually taken to be 66.7 and 60.3 pm respectively though variations occur, depending on details of the bonding and the nature of the attached atom (see also p. 292). Despite these smaller perturbations the underlying trend is clear: the covalent radius of the carbon atom becomes smaller the lower the coordination number and the higher the formal bond order.

Some properties of α-graphite and diamond are compared in Table 8.1. As expected from its structure, graphite is less dense than diamond and many of its properties are markedly anisotropic. It shows ready cleavage parallel to the basal plane, and this accounts for its flaky appearance, softness, and use as a lubricant although this latter property is due not so much to weak interplanar forces on an atomic scale as to the presence of adsorbed gases, since the coefficient of friction of graphite increases 5-fold at high altitudes and by a factor of 8 in a vacuum. By contrast, diamond can be cleaved in many directions, thus enabling many facets to be cut in gem-stones, but it is extremely hard and involatile because of the strong C–C bonding throughout the crystal. Interestingly, diamond has the highest thermal conductivity of any known substance (more than 5 times that of Cu) and for this reason the points of diamond cutting tools do not become overheated. Diamond also has one of the lowest known coefficients of thermal expansion: 1.06×10^{-6} at room temperature.

The optical and electrical properties of the two forms of carbon likewise reflect their differing structures. Graphite is a black, highly reflecting semi-metal with a resistivity $\rho \sim 10^{-4}$ ohm cm within the basal plane though this increases by a factor of ~5000 along the c-axis. Diamond, on the other hand, is transparent and has a high refractive index; there is a band energy gap of

[10] J. M. MICHELS, *Dating Methods in Archeology*, Seminar Press, New York, 1973, 230 pp., S. FLEMING, *Dating in Archeology: A Guide to Scientific Techniques*, Dent, London, 1976, 272 pp.

Table 8.1 Some properties of α-graphite and diamond

Property	α-Graphite	Diamond
Density/g cm^{-3}	2.266 (ideal) varies from 2.23 (petroleum coke) to 1.48 (activated C)	3.514
Hardness/Mohs	<1	10
MP/K	4100 ± 100 (at 9 kbar)	4100 ± 200 (at 125 kbar)
ΔH_{subl}/kJ mol^{-1}	715[a]	$\sim$710[a]
Refractive index, n (at 546 nm)	2.15 (basal) 1.81 (c-axis)	2.41
Band gap E_g/kJ mol^{-1}	—	$\sim$580
ρ/ohm cm	$(0.4-5.0) \times 10^{-4}$ (basal) 0.2–1.0 (c-axis)	$10^{14}-10^{16}$
$\Delta H_{\text{combustion}}$/kJ mol^{-1}	393.51	395.41
ΔH_f°/kJ mol^{-1}	0.00 (standard state)	1.90

[a]Sublimation to monatomic C(g).

$\sim$580 kJ mol^{-1} so that diamond has a negligible electrical conductivity, the specific resistivity being of the order $10^{14}-10^{16}$ ohm cm. (For other properties and industrial applications of diamond, see ref. 11.)

As may be seen from the heats of combustion, α-graphite is more stable than diamond at room temperature, the heat of transformation being about 1.9 kJ mol^{-1}. However, as the molar volume of diamond (3.418 cm^3) is much smaller than that of graphite (5.301 cm^3), it follows that diamond can be made from graphite by application of a suitably high pressure, provided that the temperature is also sufficiently high to permit movement of the atoms. Such transformations were first successfully achieved in 1953–5, using pressures up to 100 kbar and temperatures in the range 1200–2800 K;[2a] the presence of molten-metal catalysts such as Cr, Fe, or Ni was also found to be necessary, suggesting that the transformation may proceed via the formation of unstable metal carbide intermediates. Very recently red phosphorus has also been shown to catalyse the conversion of graphite to diamond at 77 kbar and 1800°C.[12] The use of kinetically controlled non-equilibrium processes to deposit thin films of crystalline

diamond has already been mentioned (p. 272). The relationship between the conditions for these various processes is summarized in Fig. 8.4 which shows the phase diagram of carbon near its triple point.[13] This schematic representation does not explicitly include the several carbyne-like carbon phases[7] which have been identified at very low pressures ($10^{-4}-10^{-8}$ kbar) in the region marked X.
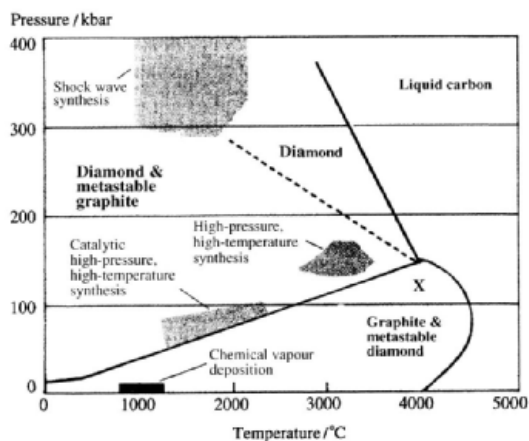

Figure 8.4 Phase diagram of carbon showing regions of importance for the production of synthetic diamond.[13]

[11] J. E. Field (ed.), *The Properties of Diamond*, Academic Press, London, 1979, 660 pp.

[12] M. Akaishi, H. Kanda and S. Yamaoka, *Science* **259**, 1592–3 (1993).

[13] P. K. Bachmann and R. Messler, *Chem. & Eng. News*, May 15, 24–39 (1989).